High-surface area graphites as supports for hydrodechlorination catalysts: Tuning support surface chemistry for an optimal performance

Eva Díaz, Salvador Ordóñez *, Rubén F. Bueres, Esther Asedegbega-Nieto, Herminio Sastre

Department of Chemical Engineering and Environmental Technology, University of Oviedo, Julián Clavería s/n, 33006 Oviedo, Spain

ABSTRACT

The performance of parent and modified high-surface area graphites (HSAGs) as supports for Pd-based hydrodechlorination catalysts is studied in this work. Catalytic hydrodechlorination of tetrachloroethylene (TTCE) has been selected as model reaction, because of its environmental relevance. Different Pd/HSAG catalysts were prepared using both parent, oxidized (using a nitric acid treatment) and pyrolysed HSAG (in order to remove the surface functional groups of the parent HSAGs). Two different preparation procedures were also tested, using either aqueous or organic solutions of the precursor (palladium chloride). Hydrodechlorination experiments have been carried out in a fixed bed reactor at 523 K, 0.5 MPa, and a space time of 24 g s mmol^{-1}. Fresh and used catalysts were characterized by TEM (metal dispersion), TPD (evolution of surface groups), TPO (amount of carbonaceous deposits), nitrogen physisorption (morphology), and XPS (chemical composition and speciation).

Obtained results show that HSAG-supported catalysts present very good performance both in terms of conversion (TOFs up to four times higher than the encountered for other conventional supports, such as activated carbon or alumina), selectivity (only small amounts of trichloroethylene being observed, in the same order of magnitude, below 10% selectivity in all the cases, that other Pd catalysts), and resistance to deactivation (more than 30 h on stream). The surface chemistry of the HSAG (concentration and type of the surface functional groups) determines both the activity of the catalyst and the main deactivation cause. Thus, catalysts prepared over the parent HSAGs show a relatively fast deactivation by fouling, ascribed to the strongest acid sites; whereas the selective removal of the surface functional groups, or the transformation of these groups during the oxidative treatment, lead to catalysts less prone to fouling. In these cases, chlorine poisoning is the main deactivation cause. The preparation procedure of the catalysts also affects their performance, being the catalysts prepared using aqueous precursors less prone to chlorine poisoning.

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1. Introduction

Tetrachloroethylene-based solvents are widely used in dry cleaning facilities and textile industries. In modern installations, the used solvent is distilled, purified tetrachloroethylene (TTCE) being reused in the process. However, the bottoms of this process have very high TTCE concentration (up to 40%), and are considered as a hazardous waste because of its high content of the organo-chlorinated compound [1]. This waste is often a sludge (containing also other organics, dust and greases) which must be solved in an organic solvent and filtered before subsequent treatments. Catalytic hydrodechlorination (HDC) is an emerging technology for the treatment of these wastes, as recently stated in both American and European technical reports [2,3]. Catalytic HDC consists of reacting the organo-chlorinated compounds with hydrogen, yielding hydrogen chloride, that can be easily removed, and, if HDC is complete, hydrocarbons, which can be burned or even recovered as valuable chemicals. HDC presents relevant environmental advantages, such as lower energy consumption and the no formation of hazardous by-products.

Although different catalysts have been tested for this reaction, supported metal catalysts are considered as the most active [4], even in the presence of high amounts of HCl (for example when un-reacted hydrogen is recycled) or when other organic compounds (such as heavier hydrocarbons, organoxygenates or small amounts of organosulfur compounds) are co-processed [5,6]. Among noble metal catalysts, palladium is the active phase providing the highest conversions and selectivities for total hydrodechlorination [7–9].

* Corresponding author. Tel.: +34 985 103 437; fax: +34 985 103 434.
 E-mail address: sordonez@uniovi.es (S. Ordóñez).

It is widely accepted that the support plays a key role on the catalyst performance, especially in the catalyst deactivation. At this point, we have studied the stability of both activated carbon [7] and alumina [5,8,9] supported palladium catalysts, determining that the formation of carbonaceous deposits is the main deactivation cause. These carbonaceous deposits lead to fast micropore blockage in the activated carbons and physical fouling of the activated phase in non-microporous materials. It has been also demonstrated in previous works that the HCl released in the reaction promotes the formation of active sites on the alumina surface that catalyse the formation of carbonaceous deposits [8]. Therefore, the ideal combination for a catalyst support will be an carbon-based non-microporous support. At this point, CNFs and CNTs are proposed as supports for hydrodechlorination or hydrogenation catalysts [10]. Graphene layers structure of these materials could minimize the coke formation and the blockage of micropores (as in the case of activated carbons) [11,12]. However, the main problem found for preparing CNF- or CNT-supported catalysts is their high chemical inertia, leading to catalysts with very poor dispersion [12,13]. In addition, the absence or low concentration of active groups in these materials lead to strongest interactions between the HCl released in the reaction and the palladium active phase, promoting chlorine poisoning.

High surface area graphites (HSAGs) are mechanically modified graphites, leading to disordered graphite layers, resulting in a marked mesoporous character and moderate surface areas (around 100–300 m^2/g). These materials have been used both as adsorbents and as catalyst supports, because of their mesoporous character. HSAGs have been also tested as supports for NO reduction [14], wet air oxidation [15], hydrogenations [16] and production of H_2 from NH_3 [17]. In these applications, it was observed that these materials show better characteristics than conventional activated carbons. These materials also exhibit high reactivity, especially because of the unsaturated valences at the edges of the graphitic layers. In the most of the HSAGs, these valences lead to the formation of oxygenated functional groups [18]. The performance of these materials as supports for palladium HDC catalysts has been compared to the performance of other carbonaceous materials, such as activated carbons or CNFs, being observed that HSAG-supported catalysts are less prone to bear carbonaceous deposits than the activated carbons and less sensitive to crystallite sintering than CNF-supported catalysts [19]. However, it must be taken into account that, because the abovementioned reasons, the surface chemistry of the HSAGs plays a key role on the metal dispersions, the catalyst performance and the deactivation mechanism. At this point, Cuervo et al. show that the kind of active sites on the HSAG surface (easy to modulate with different pre-treatment procedures) widely affect the interaction of this surface with different adsorbates [20], whereas Guerrero-Ruiz et al. indicated that the effect of the functional surface groups on the resulting dispersion of Ru and Pt catalysts is very difficult to predict, since these groups can block the interaction of the active phase with the preferential anchoring sites (edges and corners of the graphitic layers) [21]. Concerning to reaction and deactivation mechanisms, previous experiments carried out with other graphitic materials, carbon nanofibers, indicated that surface groups play a key role in reaction mechanism and into tuning deactivation effects [13].

Taking into account these facts, the scope of the present work is to perform a detailed study about the effect of the HSAG surface chemistry on the performance of the resulting catalysts. For accomplishing this scope, different activation procedures of the HSAG, preparation procedures, and metal loading were used for preparing Pd/HSAG catalysts. These catalysts were tested for tetrachloroethylene hydrodechlorination, correlating their physicochemical properties with their intrinsic activity and their deactivation behavior.

2. Experimental

2.1. Catalysts preparation

Three different HSAG samples were used as support: a commercial sample, an oxidized sample, and a sample pyrolysed in order to remove the surface groups without altering the material properties. The high surface area graphite (HSAG-300), kindly provided by Lonza (Switzerland), was used as parent material for preparing studied catalysts. In order to increase the concentration of surface functional groups, parent HSAG was refluxed in 50% nitric acid (carbon/HNO_3 = 1 g/0.01 L) at 373 K for 48 h. After that, the material was washed with doubly distilled water in a Soxhlet apparatus. Another sample of the HSAG was treated at 1173 K for 8 h, in a furnace under a helium flow (0.012 L s^{-1}), at a heating rate of 0.08 K s^{-1}, in order to remove the functional groups of the parent material. Further details about the preparation and the physico-chemical characterisation of these supports are given in a previous work [20].

Palladium catalysts were prepared over these supports by wet impregnation method, with two nominal loadings 0.5 and 1 wt%, using $PdCl_2$ as precursor. Furthermore, two preparation methods were tested: aqueous ("aq") and organic ("org") method. In both cases, $PdCl_2$ is used as precursor. For the aqueous method, $PdCl_2$ is dissolved in 0.1 N HCl to generate H_2PdCl_4, with a solution volume exceeding by 20% the pore volume of the support in each case. This solution was solved in 60 cm^3 of 0.1 N HCl and one gram of the carbonaceous material was added to this solution, where was stirred for 600 s. The excess of solvent was evaporated in a rotavapor equipped with a water bath at 343 K, spun and a vacuum pump for 1800 s. Next, the powder was dried in a furnace at 383 K for 7200 s. In the case of organic method, $PdCl_2$ was dissolved in 0.06 L of isopropanol, being the impregnation and drying steps performed as in the other case. Finally, catalysts were pelletised, crushed and sieved (selecting particles in the interval 60–100 μm) in order to ensure the absence of mass-transfer effects and high pressure drops in the catalytic bed. Catalysts were subsequently reduced in situ in H_2 at 523 K for 2 h.

2.2. Reaction studies

Reactions were carried out in a fixed bed reactor of 9 mm internal diameter an 500 mm length. More details about the catalytic reactor and operating conditions are given elsewhere [22,23]. The catalyst (in most experiments 0.25 g) was activated in situ before use by passing through the reactor 0.01 L s^{-1} (s.t.p.) of hydrogen at 523 K and 0.5 MPa for 9000 s. The catalytic experiments were carried out at 0.6 MPa and 523 K. The organic feed (toluene as solvent and tetrachloroethylene, supplied by Panreac with a minimum purity of 99.5 and 99.9%, respectively) flowed downwards through the reactor, pumped by an Alltech 525 liquid chromatography pump. A flow rate of 0.012 mL s^{-1} was fixed, with molar feed flow rate of TTCE of 0.0105 mmol s^{-1}, corresponding to a space time of 24 g s mmol^{-1} of reactant. At reaction conditions, the organic feed was completely vaporized. Hydrogen was fed co-currently, the flow rate being controlled by a Brooks 5850TR/X mass-flow regulator.

Reaction products were automatically analyzed (analytical error minor than 5%) by capillary GC in a Shimadzu GC-2010 apparatus equipped with a FID detector, using a 15 m long WCOT Silica-fused capillary column as stationary phase. Peak assignment was performed by GC-mass spectra and responses were determined using standard calibration mixtures. Once the reaction was stopped, catalysts were cooled to room temperature under nitrogen flow and stored in inert atmosphere for further characterisation.

Hydrogen chloride concentration was measured by absorption of the gas in distilled water and titration of the resulting solu-

Table 1
Morphological properties (measured by nitrogen physisorption), average crystallite size (measured by TEM and by CO chemisorption, when possible), and Pd/C, Cl/Pd and Pd^{2+}/Pd ratios measured by XPS for the fresh reduced Pd/HSAG catalysts tested in this work. Catalysts were reduced at 523 K.

Catalyst	S_{BET} ($m^2\,g^{-1}$)	Mesopore volume ($cm^3\,g^{-1}$)	d_{TEM} (nm)	d_{CO} (nm)	Pd/C	Cl/Pd	Pd^{2+}/Pd^0
0.5%Pd/HSAG-aq	271	0.43	9.3		0.5	0.5	0.5
1%Pd/HSAG-aq	223	0.27	12	15	1.2	2.4	0.6
0.5%Pd/HSAG-oxi-aq	121	0.33	6.6		0.4	1.6	0.7
1%Pd/HSAG-oxi-aq	116	0.32	6	8	0.9	0.4	1.0
0.5%Pd/HSAG-org	259	0.48	9.3		0.6	1.9	0.9
1%Pd/HSAG-org	298	0.49	14	14	1.0	0.6	0.7
0.5%Pd/HSAG-oxi-org	125	0.36	5		0.5	0.5	0.6
1%Pd/HSAG-oxi-org	126	0.34	8	9	1.1	1.1	1.3
0.5%Pd/HSAG-pyr-org	197	0.33	6.1		0.6	1.8	1.6

tion with NaOH. The mass balance of chlorine (considering the chlorine content of the TTCE feed and in the TTCE and HCl at the reactor outlet) presents closures higher than 97% in all the experiments.

The presence of both internal and external mass transfer limitations in the experiments reported in this work is discarded. These effects were experimentally (working at different particles sizes and gas velocities but keeping constant the space time) and theoretically determined in previous studies carried out with this reactive system, working at the same concentrations and operation conditions but with commercial Pd/Al_2O_3 and Pd/activated carbon catalysts of higher dispersion, internal porosity and intrinsic activity (and hence more prone to be limited by mass-transfer effects) [23].

2.3. Catalysts characterisation

The morphological characterisation of the materials, specific surface area and pore volume, was based on N_2 physisorption isotherms, determined with a Micromeritics ASAP 2020 surface analyzer. Powder X-ray diffraction (XRD) was performed with a Philips PW1710 diffractometer, working with the Cu K_α line ($\lambda = 0.154$ nm). Palladium crystallite sizes were determined by applying the Scherrer equation to the (1 1 1) crystallographic plane of Pd ($2\theta = 40.1°$). In this way, measurements of the samples were carried out in the range 2θ of 35–45°, at a scanning rate of 0.002° in 2θ min^{-1}. Likewise, the Pd particle morphology and size distributions were determined by transmission electron microscopy (TEM) in a JEOL JEM2000EXII microscope and by CO chemisorption in a volumetric Micromeritics ASAP 2020 apparatus. In the case of the used catalysts, and the catalysts with the lowest Pd loading, chemisorption measurements were not done because of experimental limitations, whereas TEM measurements were considered as accurate enough because of sharp contrast between the metallic particles and the carbonaceous material.

Carbonaceous deposits after reaction were characterized by temperature-programmed oxidation (TPO), employing a Micromeritics TPD-2900 apparatus connected to a Pfeiffer Vacuum-300 mass spectrometer. For this purpose, 10 mg carbon sample was maintained in an oxygen-stream – 2% O_2/98% He – (TPO) at 323 K for 1800 s, with a flow rate of 8.3×10^{-4} L s^{-1}, and heated from 323 to 373 K at 0.16 K s^{-1}. Coke content of the catalysts was determined based on the concentration of CO_2 in the outlet gases.

The bulk chemical composition of the fresh (reduced in H_2 at 523 K for 2 h) and used catalysts, was studied by ICP-MS, whereas surface composition was determined by X-ray photoelectron spectroscopy (XPS). XPS experiments were carried out on a SPECS-PHOIBOS system equipped with a hemispherical electron analyzer operating in a constant pass energy, using Mg K_α radiation ($h\nu = 1253.6$ eV). The samples were fixed to the sample holder using a carbon adhesive tape and analyzed without further treatments.

The background pressure in the analysis chamber was kept below 2×10^{-9} mbar during data acquisition. Since samples are conductors (could be confirmed on observing the position of the C1s peak at 284.6 eV), there was no need of applying surface neutralization during measurements. Assignation of binding energies to different atoms and oxidation states has been done according to Wagner et al. [24]. Reported quantification results reported are the average of the measurement of at least five different zones in the sample, with average errors lower than 5%.

3. Results and discussion

3.1. Characterisation of the fresh catalysts

All the supports used in this work have been thoroughly characterized in a previous paper [20], in which the use of these materials as adsorbents was studied. Surface functional groups have been determined in this work by XPS and TPD. Summarizing, parent HSAG contains a significant amount of functional groups, pyrolytic treatment lead to the total removal of the oxygenated groups, and nitric acid activation leads to a substantial increase in the concentration of these groups. The highest proportion of functional groups of both parent and oxidized supports correspond to hydroxylic groups, esters and anhydrides. The oxidative treatment increases mainly the less acidic carboxylic groups, whereas the relative concentration of strong acidic carboxylic groups and anhydrides slightly decreases after the oxidation. These treatments have not any noticeable effect on the crystallinity of the samples, although the oxidative treatments lead to a decrease in a surface area of the resulting materials (166 m^2 g^{-1} vs. 322 m^2 g^{-1}), whereas the pyrolytic treatment leads to slight surface area increases (353 m^2 g^{-1}).

The surface chemistry of the impregnated catalysts was characterized by analysis of the CO and CO_2 profiles of TPD, according to the previous reported method [20]. Desorption profiles corresponding to the CO_2 release during the TPD of the 1% Pd catalysts prepared using the parent and the oxidized HSAGs are shown in Fig. 1a and b, respectively, whereas in the case of the pyrolysed HSAG, no CO_2 releases were observed neither for the support nor for the prepared palladium catalyst. This figure shows that the addition of the active phase has not noticeable effects on the surface chemistry of the HSAGs.

The main properties of the prepared catalysts are summarized in Table 1. Active phase concentrations are in a good agreement with the nominal loadings of the catalyst. Metal dispersions were estimated from TEM micrographs, as shown in Fig. 2 for the 1% Pd catalysts studied in this work. At least 150 measured particles were used for dispersion determination, being standard deviation about 20% of the average value. XRD measurements were not introduced in Table 1, since low reproducibility in the results and high deviations from TEM values were observed (probably because the crystallite sizes are within the range of the detection limit of XRD).
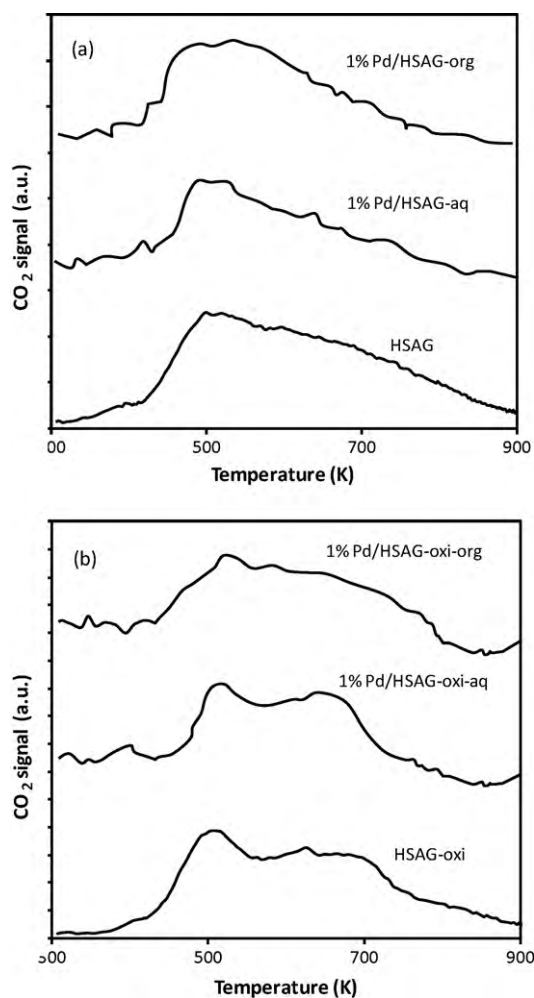
Fig. 1. CO_2–TPD profiles for the 1% Pd catalysts prepared using both aqueous and organic precursor solutions: (a) supported on parent HSAG, and (b) supported on oxidized HSAG. CO_2–TPD profiles of the supports are also provided for comparison.

Dispersion of the catalysts prepared with a loading of 1% were also measured by CO chemisorption, assuming a Pd:CO stoichiometry of 1:1. Results, also summarized in Table 1, show good agreement with the dispersion values obtained by TEM.

In all the cases, the average crystallite size increases with the palladium loading, suggesting the presence of a finite number of anchoring sites for deposition of the palladium support. As general trend, it is observed that the catalysts prepared from the oxidized support show higher dispersions than the supported on the parent support, whereas the precursor used for the impregnation seems to have a less marked effect. According to the literature findings for carbon-supported materials, this behavior seems to be related with the interaction between the palladium precursor and the electropositive carbon atoms of the functional groups [18].

Concerning to the pyrolysed graphite, it is observed that the average particle size obtained is relatively low (6.1 nm). Dispersion results obtained show important differences with other non-microporous carbonaceous materials reported in the literature. In the case of carbon nanofibers (CNFs), average crystallite diameters are higher than 20 nm using these preparation procedures (including material activation by oxidative treatments) [12,13]. Obtained results suggest that the surface chemistry of the HSAG shows an intermediate behavior between activated carbons and other graphitic materials, allowing the preparation of materials with high dispersions.

Catalyst surfaces were analyzed by XPS, obtaining data of surface Pd concentration, Cl/Pd and Pd^{2+}/Pd^0 (Table 1). Chlorine was detected in all the samples, appearing in the binding energy region of inorganic chlorine (198–199 eV). Chlorine is considered as catalysts sintering or poisoning promoter; however, in our case, this contribution seems to be irrelevant in comparison to HCl amounts released during the reaction. The pretreatment of the HSAG also plays an important role on the electronic state of the active phase. The molar fraction of Pd^{2+} is usually higher in the catalysts prepared from the oxidized support, although all the catalysts were reduced at the same temperature and the catalysts supported on the oxidized support show highest dispersion. This result suggests that the support functional groups stabilize the oxidized forms of the active phase. Additional reduction procedures were
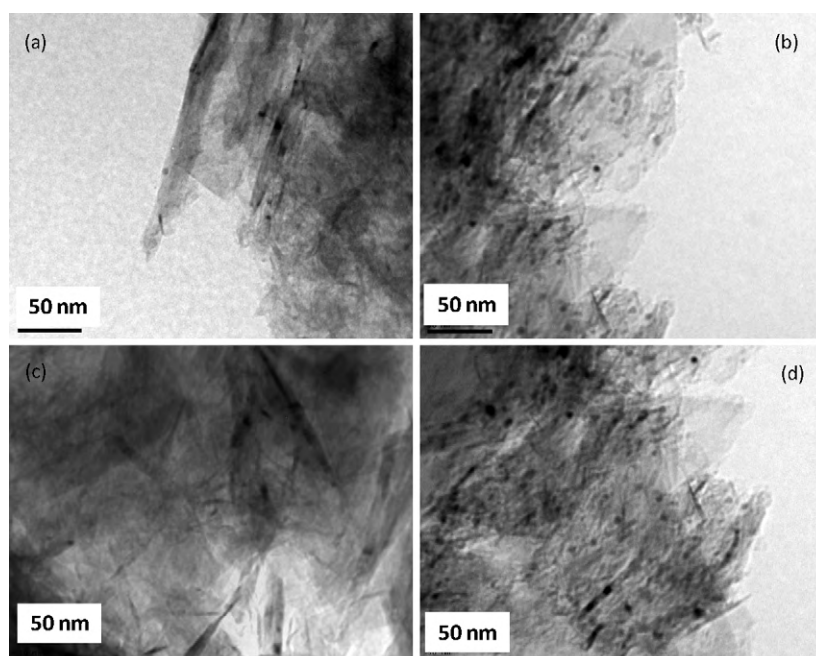

Fig. 2. Representative TEM micrographs of the 1% Pd loaded catalysts used in this work: Pd/HSAG-aq (a), Pd/HSAG-org (b), Pd/HSAG-oxi-aq (c) and Pd/HSAG-oxi-org (d).
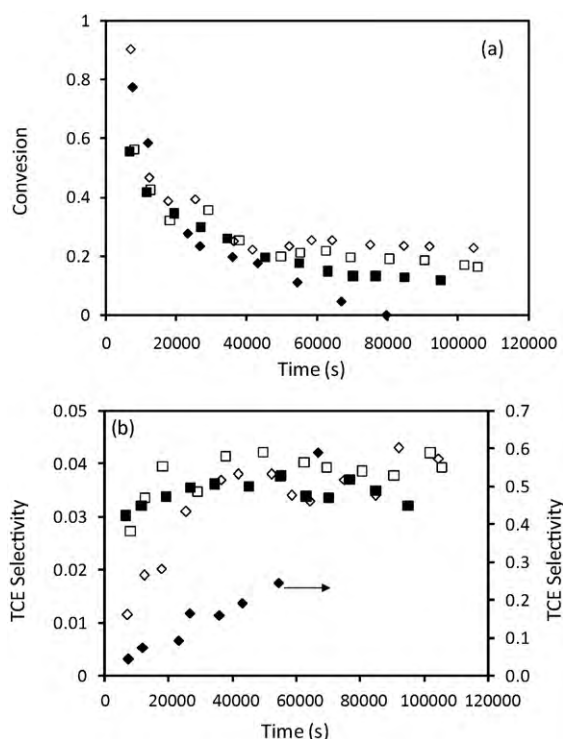
Fig. 3. Evolution of the conversion (a) and selectivity towards trichloroethylene (b), with the time on stream for the hydrodechlorination of TTCE at 523 K over the catalysts with 1% of Pd loading: Pd/HSAG-aq (◆), Pd/HSAG-org (■), Pd/HSAG-oxi-aq (◇) and Pd/HSAG-oxi-org (□).

tested, changing reduction times (up to 18,000 s) and temperatures (up to 623 K, in order to not significantly modify support chemical properties), being observed the presence of Pd^{2+} in all the cases.

3.2. Catalytic performance

Pd/HSAG catalysts were tested in the hydrodechlorination of tetrachloroethylene, catalyst performance is expressed in terms of conversion of TTCE, defined as the percentage of TTCE fed to the reactor which is reacted. Fig. 3 shows the evolution of the conversion and selectivity for trichloroethylene (the only organochlorinated by-product detected in all the cases) with the time on stream for the catalysts with 1 wt% of Pd. All the curves reported in this figure have been replicated in order to ensure the reproducibility of the obtained data. In general terms, good reproducibility has been observed, even for catalysts prepared in different batches. It is observed a relatively high initial conversion, followed by a period of fast deactivation and a constant activity period. In several cases (especially when using the parent graphite and aqueous precursor), fatal deactivation of the catalysts was observed.

Concerning to the catalysts prepared with the highest metal loading (Fig. 3), it is observed that, although all the catalysts present similar performance at the beginning, catalysts prepared using oxidized supports present a more stable performance. Therefore, the deactivation rate follows the order: 1%Pd/HSAG-aq (yielding complete deactivation) > 1%Pd/HSAG-org > 1%Pd/HSAG-oxi-org ≈ 1%Pd/HSAG-oxi-aq. It is remarkable that both catalysts prepared from the oxidized supports yield conversions higher than 20% after 20 h on stream.

The only differences observed with the catalysts prepared with the 0.5 wt% Pd (Fig. 4) are the highest initial activity of the catalysts prepared form oxidized support. For these supported catalysts, it
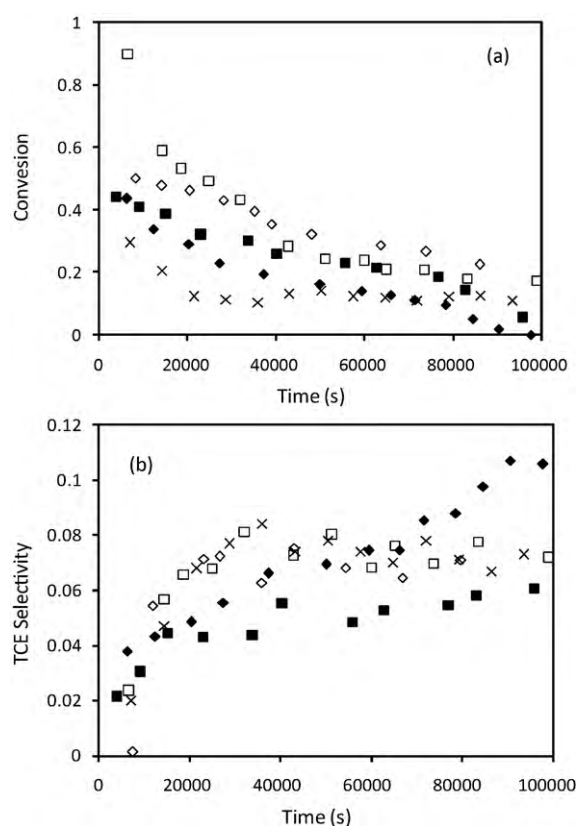

Fig. 4. Evolution of the conversion (a) and selectivity towards trichloroethylene (b), with the time on stream for the hydrodechlorination of TTCE at 523 K over the catalysts with 0.5% of Pd loading: Pd/HSAG-aq (◆), Pd/HSAG-org (■), Pd/HSAG-oxi-aq (◇), Pd/HSAG-oxi-org (□), and Pd/HSAG-pyr-org (×).

is observed both the highest initial activity and the highest stability, especially in the case of the catalyst prepared from organic precursor. This different behavior is caused by the highest concentration of Pd^0 in these catalysts (reduction is more efficient at low metal loadings), as observed in Table 1 and as it will be explained in higher detail in the next section. It should be also noted that, although the used precursor has not any noticeable influence in the catalyst performance for the catalysts prepared using oxidized support, the catalysts prepared using parent HSAG and aqueous precursor present markedly lower stability than the catalysts prepared using organic precursor and parent support. Regarding to the catalyst prepared pyrolysed support, it present lower initial activity but present very stable performance.

The other point to be considered in the efficiency for total hydrodechlorination is the selectivity for total dechlorination. At this point, the only chlorinated by-product detected was trichloroethylene, in good agreement with the observed when this reaction is performed over different kind of catalysts [4–9,25]. At this point, we have observed in previous works, that the reactivity of the chloroolefins increases in the order TTCE < TCE ≪ dichloroethylenes, therefore justifying the absence of di- and monochloroolofins in the reaction products [23]. If the performance of the different HSAG-supported catalysts is compared, it is observed that the selectivity towards partial hydrodechlorination compounds is higher for the 0.5% Pd loaded catalysts.

Concerning the influence of the support or the preparation method, no significant differences where found for the 1% Pd catalysts (except for the Pd/HSAG-aq, but this catalyst is completely deactivated) whereas for the 0.5% Pd catalysts, the catalyst prepared using the parent support present the highest selectivities for total dechlorination (this effect is clearly observed for the cat-
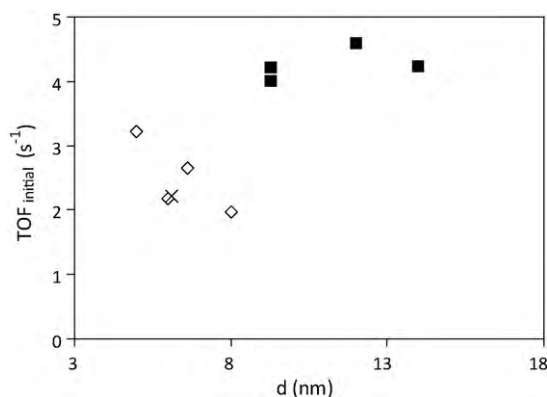
Fig. 5. TOF for fresh catalysts on parent (■), oxidized (◊), and pyrolysed (×) supports as a function of the particle diameter.

alyst prepared from organic precursor, whereas it is overlapped for the catalyst prepared from aqueous precursor because of the fast deactivation). This result suggests again that higher dispersions lead to lower selectivities for the total dechlorination. In a previous work, we have proposed a mechanism for this reaction based on successive changes between Pd^{2+} (specimen that interact with the chlorinate olefin and that is generated by the reaction of the HCl released during the reaction) and the Pd^0 (responsible of the activation of the hydrogen) [13]. As the reaction is performed in a hydrogen-rich environment, it is expected that higher dispersions lead to a catalyst more difficult to reoxidise, so that the four successive oxidation–reduction cycles needed for the total dechlorination are more difficult for being completed. So, the highest selectivities for total dechlorination (both considering HSAG and other carbonaceous supports) are obtained with moderate dispersions.

Concerning to the chemical reaction of the toluene, very small amounts of methyl-cyclohexanes were observed in the first hours of reaction, being this reaction completely stopped after 4 h on stream. No chlorinated derivatives of toluene were formed under these reaction conditions.

Results corresponding to the fresh catalysts, obtained from the deactivation curves and extrapolating to $t = 0$, can be analyzed in terms of TOF values (mol of TTCE converted per second and exposed palladium atom). Fig. 5 shows the evolution of the initial TOFs with the metal dispersion. Important differences were observed depending on the activation of the support. Catalysts prepared from parent HSAGs present the typical profile of a structure-insensitive reaction, being the TOF values completely independent from the metal dispersion. This result is a good agreement with the findings reported by Ribeiro et al. [26] for the hydrodechlorination of chlorofluorocarbons over Pd catalysts. By contrast, other authors, as well as our own works with CNFs-supported Pd catalysts suggest that the hydrodechlorination can be a structure-sensitive reaction. Concerning to the catalysts prepared from the oxidized support, it is observed an apparent positive structure-sensitiveness effect, higher particles leading to lower intrinsic activity. This result suggests that there is another effect (such as the oxidation state of the Pd or support-active phase interactions) overlapping this one.

The evolution of the initial TOFs with both the Cl total concentration and the Pd^{2+}/Pd^0 ratio, both measured by XPS, are shown in Fig. 6. These parameters show very different effects on catalyst performance. For each support, no trend of the initial TOFs values was observed, remaining the TOF almost constant at different values of the Cl/Pd ratio. The role of chloride ions in chemical reactions involving Pd has been widely studied in the literature [27], being accepted that chloride ions can act as catalyst poison but also that
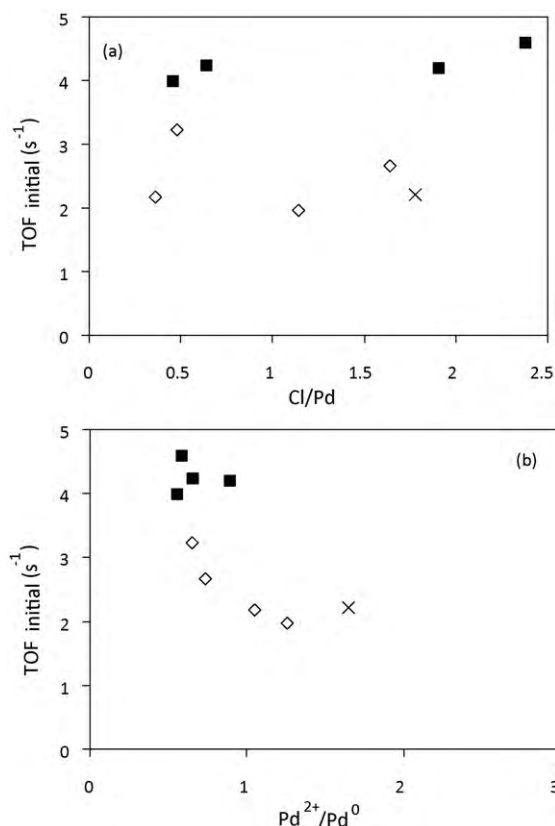

Fig. 6. TOF for fresh catalysts on parent (■), oxidized (◊), and pyrolysed (×) supports as function of the Cl/Pd ratio (a) and Pd^{2+}/Pd^0 ratio (b).

the presence of this ions are necessary for the catalytic cycle, as explained in detail in [13].

The situation is different in the case of the Pd^{2+}/Pd ratios. In the case of the parent support, this parameter has not any noticeable effect on the reaction TOF (it should be noted that this ratio present a very slight variation for these materials), whereas in the case of the oxidized supports, TOF values clearly increase as the Pd^{2+}/Pd ratio decreases. If it is also considered that the catalysts prepared using the oxidized support have, in general terms, the highest concentration of the oxidized species, the fraction of reduced Pd in the catalyst is lower than the optimal value. At this point, it is accepted that although Pd is the catalytic active phase, the presence of Pd^{2+} is necessary for accomplishing the catalytic cycle [13]. Therefore, different optimal Pd^{2+}/Pd ratios are reported in the literature, depending on the chlorinated compound and the support. Gomez-Sainero et al. [28] reported optimal values of about 1.5. In a previous work, using different CNF as catalyst supports, it was observed that the optimal ratio was between 0.3 and 0.7, the lower optimal ratios corresponding to most inert support [13]. This trend can be also guessed for the HSAG support, but in this case, the optimal ratio seems to be below the minimal concentration of Pd^{2+} of the studied catalysts. The differential behavior of both kinds of HSAG supports, as well as the differences among the different carbonaceous supports, must be explained in terms of the dispersion (small crystallites of active phase, enhances the reduction of the Pd^{2+} species so being needed higher concentration of Pd^{2+} for accomplishing the catalytic cycle) and the stabilizing effect of the oxygenated functional groups over the oxidized metal species. Concerning to the catalyst prepared over the pyrolysed HSAG, it shows the highest Pd^{2+}/Pd ratio and its TOF values is among the lowest.
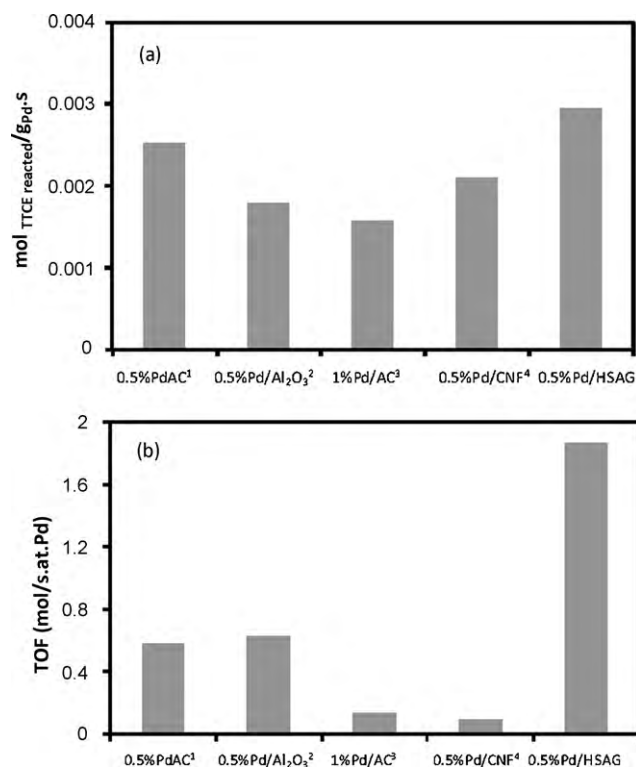
Fig. 7. Comparison of the performance of the Pd/HSAG-org catalyst and other Pd catalysts tested for TTCE hydrodechlorination in the same reaction conditions: (1) commercial Pd/activated carbon [7], (2) commercial Pd/Al₂O₃ [8], (3) home-made Pd/activated carbon [19], and (4) home-made Pd/CNF [13]. Comparison is given in terms of: (a) specific activity (mol of TTCE reacted per second and gram of Pd), and (b) TOF (considering the metal dispersion).

Fig. 8. Crystallite size distribution for the 1%Pd/HSAG-aq fresh (a) and after reaction (b).

to alumina-supported catalysts, but markedly longer than all the other carbon-supported catalysts [8,12,19].

3.3. Characterisation of the catalytic deactivation

Samples of catalysts after 108,000 s on stream were characterized by different techniques in order to establish the main deactivation causes. The main characterisation results are shown in Table 2. The evolution of the crystallite size presents three different trends. The catalyst prepared on pyrolysed support exhibits an important sintering effect, suggesting that the absence of functional groups increases the metal coalescence. Catalysts impregnated on the parent support exhibit a redistribution of the metal, increasing the Pd dispersion (about two-three times), as observed in Fig. 8 for the case of the 1% Pd/HSAG-aq catalyst. This fact could be the result of different effects: the effect of functional groups avoiding the sintering [13,27], and the redispersion of the metal crystallites by the hydrogen chloride released in the reaction [29]. Finally, the oxidized supported catalysts show a more stable crystallite size during the reaction-excepting for 1% Pd/HSAG-oxi-aq which increases considerably. The oxidized support presents a higher con-

The overall performance of these materials is compared with the corresponding to other materials reported in the literature [7,8,13,19] in Fig. 7. Comparisons are made in terms of mol of TTCE converted per atom of Pd in the catalysts (Fig. 7a), and also as TOF value (Fig. 7b). Values reported in these Fig. 7 correspond to 5 h on stream at the same reaction conditions that the deactivation experiments performed in this work. The selected time-on-stream corresponds to the activity plateau of all the reported catalysts. It is observed that the performance of the HSAG-supported catalysts is in general terms better than the corresponding to commercial Pd/Al₂O₃ and Pd/C catalysts, as well as to other carbon-supported Pd catalysts (as CNF-supported). This difference in TOF values can be understood not only due to the relatively high dispersion of these catalysts, but also considering the support, that plays an important role on its performance. From the point of view of the resistance to the deactivation, the best HSAG-supported catalysts present periods of constant activity similar to the corresponding
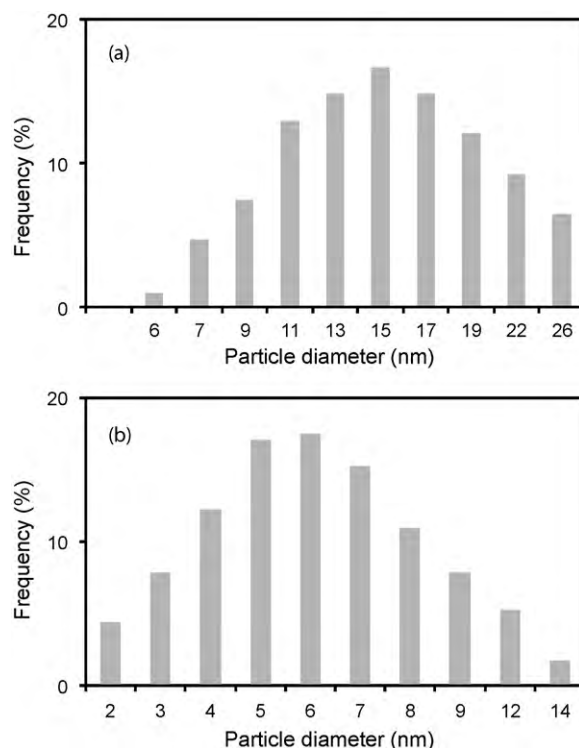
Table 2
TEM average crystallite diameter, average pore diameter (BJH-desorption), Cl/Pd (w/w ratio, considering the total chlorine concentration), Pd²⁺/Pd⁰ ratio, ratio of inorganic (binding energy between 198 and 199 eV) and organic (binding energy between 199.5 and 201 eV) chlorine, percentage of coke and combustion temperature of coke for the studied catalysts after 108,000 s on stream at 523 K and 0.5 MPa.

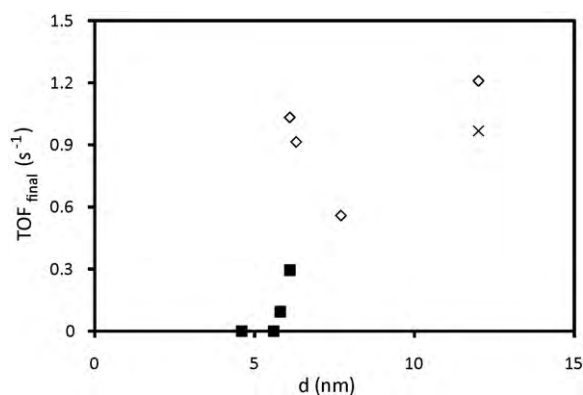| Catalyst	d_{TEM} (nm)	Avg. pore diameter (nm)	(Cl/Pd) used	(Pd²⁺/Pd) used	(Cl$_{in}$/C$_{org}$) used	%Coke	T_{comb} (K)
0.5%Pd/HSAG-aq	5.6	7.0	22.1	10.8	0.6	1.6	714
1%Pd/HSAG-aq	5.3	6.2	4.0	2.6	0.4	4.8	723
0.5%Pd/HSAG-oxi-aq	6.1	14	33.4	5.1	0.8	0	–
1%Pd/HSAG-oxi-aq	12	9.9	9.3	2.8	0.8	0	–
0.5%Pd/HSAG-org	5.8	7.2	66.1	8.3	0.6	1.4	682
1%Pd/HSAG-org	6.1	7.7	60.0	7.9	0.3	1.5	688
0.5%Pd/HSAG-oxi-org	6.3	13.1	38.2	5.8	0.9	0	–
1%Pd/HSAG-oxi-org	7.7	10.1	45.1	6.8	1.9	0	–
0.5%Pd/HSAG-pyr-org	12	12.3	38.62	6.3	1.2	0	–

Fig. 9. TOF of catalysts on parent (■), oxidized (◇), and pyrolysed (×) supports as function of the particle diameter, after 108,000 s on stream.

centration of oxygen surface groups but, according to Calvo et al. [30], only the CO_2-evolving groups are determinant for metal dispersion. These groups correspond to the strongest acidic carboxylic groups, whose relative concentration decreases after the oxidative treatment (this treatment increases the total concentration of functional groups, but this effect is more marked for the non-carboxylic groups). Thus, the incorporation of an additional amount of oxygen surface groups by the oxidative treatment, decreasing the acidity strength, do not contribute to increase the metal dispersion. A similar behavior was observed for Pd/CNF catalysts [13], where the presence of functional groups decreases the sintering effect—in comparison to parent CNF, whose functional groups concentration was negligible. Finally, the higher relative concentration of Pd^{2+} species can also hinder metal redispersion.

If the residual TOFs (calculated from the conversion and the Pd dispersion measure after 108,000 s on stream) are correlated with the average particle sizes of the used catalysts (Fig. 9), it is observed that increases in the particle size leads to catalysts with higher residual activity, no systematic trends being observed. This behavior and the lower TOF values observed for the aged catalysts for all the studied catalysts suggest that the sintering is not the main deactivation cause.

If the presence of coke deposits is considered, the behavior of the catalysts during the deactivation is completely different depending on the selected support (parent, oxidized or pyrolysed HSAG). In the case of the experiments performed with the parent HSAG, significant amounts of coke deposits were found in the used catalysts. During the TPO of these catalysts (shown in Fig. 10, for the case of the catalysts prepared from organic precursor), two peaks (for the CO_2 evolved) are observed for the used catalysts prepared from the parent support: the main peak, at around 1000 K, corresponding to the combustion of the bulk support; whereas the other peak (600 K) corresponds to the burning of carbonaceous deposits [5]. At this point, a reported study on the formation of carbonaceous deposits on Ni/SiO2 catalysts from polychloroolefins, suggests combustion temperatures in the interval 600–900 K for these coke deposits [31]. It should be noted that TPO analyses of the supports were carried out in a previous work [20], being observed in all the cases the presence of only one bulk combustion peak (similar to the second peak observed in Fig. 10). The coke deposits combustion peaks are not observed in the catalysts prepared from both pyrolysed and oxidized support, suggesting that these catalysts do not bear carbonaceous deposits. Concerning to the effect of the preparation method, the catalyst prepared from aqueous precursor present higher coke deposits loading, specially the catalyst with 1% of Pd loading (catalyst presenting fatal deactivation at the reaction conditions).
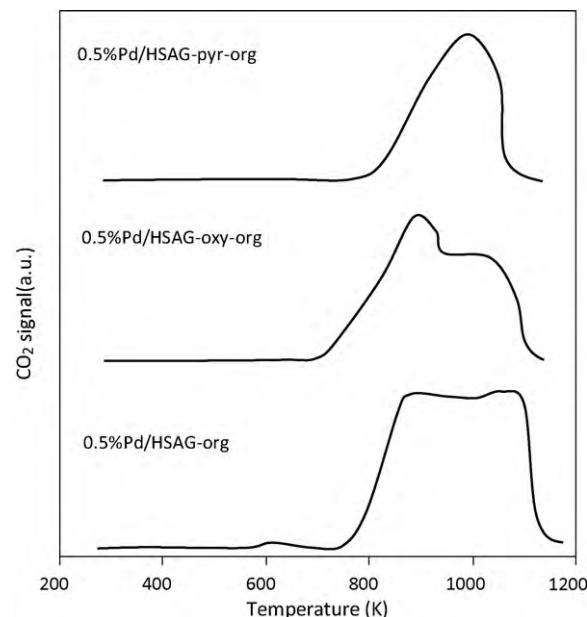

Fig. 10. CO_2 release profile during TPO of the used 0.5%Pd/HSAG-org, 0.5%Pd/HSAG-oxy-org, 0.5%Pd/HSAG-pyr-org catalysts. Heating rate: 0.16 K s^{-1}.

The presence of these carbonaceous deposits has important consequences on the morphology of the supports. The pore size distributions of the catalysts presenting coke formation are significantly narrowed, decreasing the average pore diameter (Table 2). Thus, catalysts supported on parent HSAG, which form coke during the reaction, show a drastic reduction in the mesopore volume, blocking the active sites. In good agreement with this fact, all the catalysts showing fatal deactivation are prepared using the parent HSAG. Concerning the deactivation by coke, both the highest dispersion of Pd on parent supported catalysts and the presence of the strongest acidic groups could enhance the formation of coke. By contrast, weak acid sites present at higher concentrations in the oxidized supports can promote hydrogen spill-over, contributing to minimize the formation of coke deposits. In the case of the strong acid sites, this effect is either not so marked or it is overlapped because of this sites can catalyse reactions leading to coke formation. The synergy between weak acid sites and palladium for promoting hydrogen spill-over has been demonstrated for the case of Pd/CNF materials [32], using thermogravimetric analysis of hydrogen adsorption.

Changes on surface chemistry were determined by XPS. This technique allows a quantification of Pd and Cl species, as well as a speciation between the chemical environments of these species. The surface concentration of palladium (also verified for the case of the bulk composition using ICP-MS) is very similar to the corresponding to the fresh catalysts, discarding the active phase leaching during the reaction. However, there are important differences in the oxidation state of the Pd atoms between the fresh and used catalysts. The concentration of Pd^{2+} species increases markedly – between three and 20 times – for the deactivated catalysts. In general, the increase on the Pd^{2+} fraction between fresh and used catalyst depends on the dispersion of the fresh catalyst. Higher dispersion leads to higher palladium oxidation. Concerning to the effect of the HSAG treatment or preparation procedure, no clear conclusion can be obtained about the effect on this parameter on the oxidation easiness. The increase of the Pd^{2+}/Pd^0 ratio during hydrodechlorination reactions has been found by other authors over a vast amount of supports and reaction mediums. This high stability of electron-deficient palladium species in reductive envi-

ronments when chloride and protons ions are present in the solid – from the point of view of the redox potentials for the H^+/Pd pair – has already been reported [27]. This behavior could be caused by the interaction of Pd^0 with neighbouring protons, coming from the HCl generated during the reaction. The presence of chloride ions stabilizes this system, hence promoting the oxidation. This effect has been proposed in the literature both for hydrodechlorination reactions and for explaining the ab-normal reduction properties of catalysts prepared from chlorine-containing precursors [27].

The other point to be considered is the increase of chlorine concentration. Considering that HCl is continuously released during the reaction, used catalysts trend to bear higher amounts of chlorine than fresh catalyst. This effect is, in general terms, more marked for the catalysts with lower metal loading, indicating that it is controlled by the chemistry of the support rather than for the metal. The highest chlorine concentrations are observed for the catalysts prepared using the parent HSAGs and organic Pd precursor. The XPS analyses of Cl 2p allow to distinguish between inorganic chlorides, associated to the metal active phases (198.8 eV), and organic chloride chlorine covalently bonded to carbon (200 eV). Concerning to the organic chlorine, it should be taken into account that, according to Brichka et al. [33], chloride anions thoroughly intercalated in defects of graphene layers present binding energies close to the corresponding to organic chlorine. By this reason, even the catalysts not bearing carbonaceous deposits present significant concentration of this "organic" chlorine.

The total amount of chlorine and the ratio between both kinds of chlorine atoms is also summarized in Table 2. It is observed that the Pd/HSAG catalysts prepared using the organic precursor, were the catalysts with higher chlorine surface concentration, and the catalysts with higher ratio of organic chlorine, in good agreement with the important amount of carbonaceous deposits they are bearing.

A plot of the residual TOF versus de chlorine concentration and the Pd^{2+}/Pd ratio is depicted in Fig. 11. It is observed that the shape of the curves is very similar, indicating that both parameters are closely correlated. The only exceptions for this behavior were the points corresponding to the total deactivation of the catalysts, this deactivation being caused by coke deposition. This analogy suggests a poisonous effect of the chlorine leading to a subsequent oxidation of the Pd. Two different trend lines were clearly observed for the catalysts: in the case of the catalysts prepared using the oxidized supports, the decrease of the final TOF is well correlated with increases in the chlorine concentration and oxidized Pd fraction. This fact, in agreement with the absence of carbonaceous deposits, suggests that chlorine poisoning, caused by the HCl released during the reaction, is the main deactivation cause. Thus, the best performance observed for the catalysts prepared using aqueous precursor (Figs. 3 and 4) is related to the lower trend of these catalysts to form metal chlorides (as evidenced from the lower Cl and Pd^{2+} contents). The interaction of polar gases with catalytic active phases strongly depends on the chemistry of the supports. In general, supports with polar groups, such as hydroxides in the case of inorganic supports or surface functional groups in the case of carbonaceous materials, can interact with polar inorganic species, concentrating these species in the support and avoiding their interaction with the active phase. These effects are considered in the literature, for example, for explaining the high sulfur poisoning resistance of alumina-supported catalysts for methane oxidation in presence of SO_2 [34]. For the specific case of the interaction of chloride ions with graphitic materials, it has been demonstrated that surface functional groups play a key role on the adsorption of chlorine species [35,36]. Concerning to the differential behavior of the catalysts prepared using aqueous Pd precursors, it can be also justified, considering that the treatment
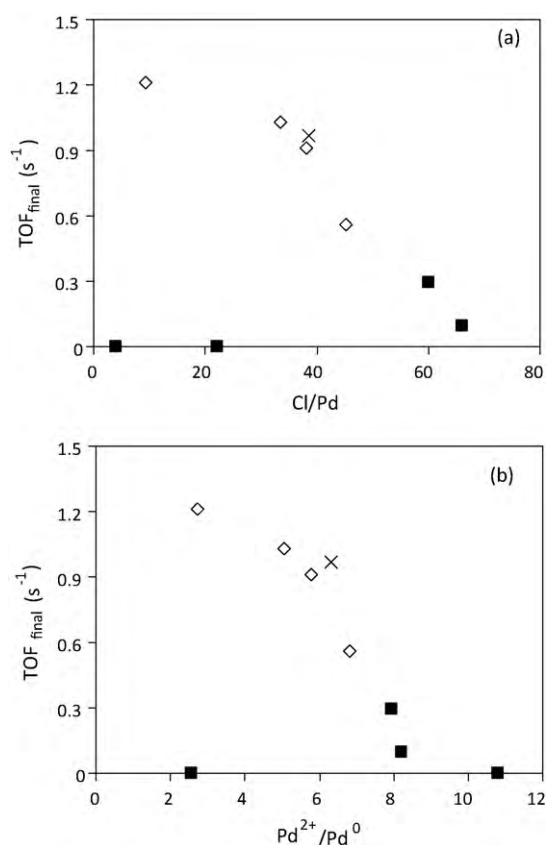

Fig. 11. TOF of catalysts on parent (■), oxidized (◇), and pyrolysed (×) supports as function of: Cl/Pd ratio (a), and Pd^{2+}/Pd^0 ratio (b), after 108,000 s on stream.

with an aqueous solution increases the polarity of the functional groups [13].

On the other hand, the catalysts prepared from the parent support do not follow a homogeneous trend, since the catalysts prepared using aqueous precursor are completely deactivated presenting low Cl/Pd ratios (the fast deactivation lead to the formation of lower amounts of hydrogen chloride than for the other catalysts). The catalyst prepared from the pyrolysed support, falls in the abovementioned trend, suggesting again that chlorine-poisoning is the main deactivation cause.

4. Conclusions

High-surface area graphites (HSAGs) are very promising supports for Pd-based hydrodechlorination catalysts. In the case of TTCE hydrodechlorination, these materials exhibit even better performance (both in terms of intrinsic activity and resistance to deactivation) than other supports studied in the literature (such as activated carbons, alumina or carbon nanofibres).

However, the chemistry of the support plays a key role on the performance of the catalysts, and, more markedly in their deactivation behavior. Thus, the strong acid sites present in the parent HSAG promote the formation of coke, whereas the transformation of these centers in other functionalities through an oxidative treatment, or just the removal of these sites, lead to catalyst less prone to bear carbonaceous deposits. In these last cases, the chlorine poisoning is the main deactivation cause; the preparation technique also playing a key role in this deactivation behavior. In this case, catalysts prepared from aqueous solutions of precursors show a better behavior.

Acknowledgements

References

[1] Toxicological Profile for Trichloroethylene and Tetrachloroethylene, Agency for Toxic Substances and Disease Registry (ATSDR), Department of Health and Human Services, Public Health Service, Atlanta, GA, 1997.
[2] European Commission, Reference Document on Best Available Techniques for Waste Treatment, European Commission, Seville, 2005, Available at: http://eippcb.jrc.es/pages/FActivities.htm.
[3] Toxics Release Inventory, Public Data Release, USEPA, Office of Environmental Information, Washington, DC, 2001.
[4] S. Ordoñez, F.V. Díez, H. Sastre, Appl. Catal. B 25 (2000) 49.
[5] E. López, S. Ordóñez, F.V. Díez, Appl. Catal. B 62 (2006) 57.
[6] E. López, F.V. Díez, S. Ordóñez, Appl. Catal. B 82 (2008) 264.
[7] S. Ordóñez, F.V. Díez, H. Sastre, Appl. Catal. B 31 (2001) 113.
[8] S. Ordóñez, F.V. Díez, H. Sastre, Appl. Catal. B 40 (2003) 119.
[9] S. Ordóñez, H. Sastre, F.V. Díez, Thermochim. Acta 379 (2001) 25.
[10] C. Amorim, G. Yuan, P.M. Patterson, M.A. Keane, J. Catal. 234 (2005) 268.
[11] Q. Liu, Z.M. Cui, Z. Ma, S.W. Bian, W.G. Song, J. Phys. Chem. C 112 (2008) 1199.
[12] R.F. Bueres, E. Asedegbega-Nieto, E. Díaz, S. Ordóñez, F.V. Díez, Catal. Commun. 9 (2008) 2080.
[13] S. Ordóñez, E. Díaz, R.F. Bueres, E. Asedegbega-Nieto, H. Sastre, J. Catal. 272 (2010) 158.
[14] C. Marquez-Alvarez, I. Rodríguez-Ramos, A. Guerrero-Ruiz, Carbon 34 (1996) 339.
[15] P. Gallezot, S. Chaumet, A. Perrad, P. Isnard, J. Catal. 168 (1997) 104.
[16] B. Bachiller-Baeza, A. Guerrero-Ruiz, P. Wang, I. Rodríguez-Ramos, J. Catal. 204 (2001) 450.
[17] R.Z. Sorensen, A. Klerke, U. Quaade, S. Jensen, O. Hansen, C.H. Christensen, Catal. Lett. 112 (2006) 77.
[18] C.A. León y León, L.R. Radovic, in: P.A. Thrower (Ed.), Chemistry and Physics of Carbon, vol. 24, Dekker, New York, 1994, p. 213.
[19] R.F. Bueres, E. Asedegbega-Nieto, E. Díaz, S. Ordóñez, F.V. Díez, Catal. Today 150 (2010) 16.
[20] M.R. Cuervo, E. Asedegbega-Nieto, E. Díaz, S. Ordóñez, A. Vega, A.B. Dongil, I. Rodríguez-Ramos, Carbon 46 (2008) 2096.
[21] A. Guerrero-Ruiz, P. Badenes, I. Rodríguez-Ramos, Appl. Catal. A 173 (1998) 313.
[22] S. Ordóñez, H. Sastre, F.V. Díez, J. Hazard. Mater. 81 (2001) 103.
[23] S. Ordóñez, F.V. Díez, H. Sastre, Ind. Eng. Chem. Res. 41 (2002) 505.
[24] C.D. Wagner, W.M. Riggs, L.E. Davis, J.F. Moulder, G.E. Muilemberg, Handbook of X-ray Photoelectron Spectroscopy, Perkin Elmer Corp., Eden Prairie, MI, 1979.
[25] N.C. Concibido, T. Okuda, W. Nishijima, M. Okada, Appl. Catal. B 71 (2007) 64.
[26] F.H. Ribero, C.A. Gerken, G. Rupprechter, G.A. Somorjai, C.S. Kellner, G.W. Coulston, L.E. Manzer, L. Abrams, J. Catal. 176 (1998) 352.
[27] Z. Karpinski, Adv. Catal. 37 (1990) 45.
[28] L. Gomez-Sainero, X.L. Seoane, J.L.G. Fierro, A. Arcoya, J. Catal. 209 (2002) 279.
[29] K. Foger, D. Hay, J. Jaeger, J. Catal. 96 (1995) 154.
[30] L. Calvo, M.A. Gilarranz, J.A. Casas, A.F. Mohedano, J.J. Rodríguez, Appl. Catal. B 67 (2006) 68.
[31] A. Nieto-Marquez, J.L. Valverde, M.A. Keane, Appl. Catal. A 332 (2007) 237.
[32] E. Díaz, M. León, S. Ordóñez, Int. J. Hydrogen Energy 35 (2010) 4576.
[33] S.Y. Brichka, G.P. Prikhod'ko, Y.I. Sementsov, A.V. Brichka, G.I. Dovbeshko, O.P. Paschuk, Carbon 42 (2004) 2581.
[34] S. Ordóñez, P. Hurtado, H. Sastre, F.V. Díez, Appl. Catal. A 259 (2004) 41.
[35] M. Gurrath, T. Kuretzky, H.P. Boehm, L.B. Okhlopkova, A.S. Lisitsyn, V.A. Likholobov, Carbon 38 (2000) 1241.
[36] J. González, M. del, C. Ruiz, A. Bohé, D. Pasquevich, Carbon 37 (1999) 1979.